

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MITSUBISHI CHEMICAL CORP

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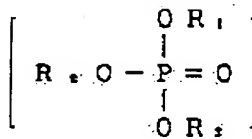
(72)Inventor : UE MAKOTO

(54) FLAME RETARDER OF ELECTROLYTE FOR LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte having flame retardance while maintaining battery characteristics by including trialkyl phosphate.

SOLUTION: Trialkyl phosphate giving flame retardance to an electrolyte is represented by formula I. In the formula, R1-R3 are the same or different straight-chain or branched alkyl group having 1-4 carbon atoms. Specifically trimethyl phosphate and dimethyl phosphate may be mentioned. The content of the phosphoric ester in the electrolyte depends on the capacity requirement of a battery, but when the whole amount of the solvent is replaced by the phosphoric ester, the flame retardance of the battery is maximized. For increasing the flame retardance by adding to the electrolyte as an assistant solvent, 15 wt.% or more phosphoric ester is preferable, and addition of 30 wt.% or more phosphoric ester is more preferable. As the solvent for mixing, ethylene carbonate, for example, is mentioned.



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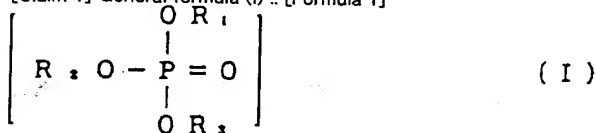
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CLAIMS

[Claim(s)]

[Claim 1] General formula (I) : [Formula 1]



(— R₁–R₃ are the alkyl groups of the shape of a straight chain of carbon numbers 1–4 which may differ even if mutually the same, and the letter of branching among a formula Flameproofing agent of the electrolytic solution for lithium cells which is shown by) and which is trialkyl phosphate.

[Claim 2] The flameproofing agent according to claim 1 R₁–whose R₃ are methyl groups.

[Claim 3] The method of carrying out flameproofing of the electrolytic solution for lithium cells of making a flameproofing agent according to claim 1 or 2 containing 15% of the weight or more in the solvent of the electrolytic solution.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the electrolytic solution used for a lithium cell. According to this invention, the high lithium cell of safety can be obtained.

[0002]

[Description of the Prior Art] Conventionally, independent or the things which dissolved solutes, such as a lithium perchlorate, lithium fluoride, lithium lithium fluoride, and a trifluoromethane sulfonic-acid lithium, in these mixed solvents, such as propylene carbonate, gamma-butyrolactone, 1, and 2-dimethoxyethane, are used for the lithium cell as the electrolytic solution.

[0003] On the other hand, the organic compound which contains lithium or a halogen in a molecule at inorganic compound rows, such as an antimony oxide and boric-acid zinc, is known as a flameproofing agent. However, in case fire retardancy is given to the electrolytic solution, it is necessary not to bar the fundamental performance as the electrolytic solutions, such as conformity, between conductivity, the operating potential range, operating temperature limits, and an electrode material. For example, in almost all cases, an above-mentioned inorganic compound and an above-mentioned halogenide are a solid matter, are insoluble to an organic solvent, and reduce conductivity. Moreover, halogenated hydrocarbons, such as a methylene chloride currently generally used as an organic solvent, have a low dielectric constant, and since conductivity is reduced, they cannot be used as a solvent used for the electrolytic solution.

[0004]

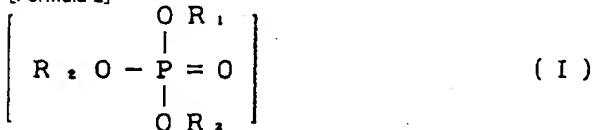
[Problem(s) to be Solved by the Invention] Since the solvent which is very easy to burn is being used for the above-mentioned lithium cell, when a cell breaks by the internal short circuit etc., it ignites to the electrolytic solution, and a device may be damaged or sparks may result in a fire. Especially, a lithium cell comes to be carried in a portable equipment, and the safety of a lithium cell is changing importance with increase and a social problem increasingly in recent years.

[0005]

[Means for Solving the Problem] Maintaining the property as a cell by using low-grade phosphoric ester as the solvent or assistant solvent of the electrolytic solution, he succeeded in obtaining the electrolytic solution which shows fire retardancy, and this invention person completed this invention.

[0006] That is, this invention is general formula (I): [0007]

[Formula 2]



[0008] (— R₁—R₃ are the alkyl groups of the shape of a straight chain of carbon numbers 1—4 which may differ even if mutually the same, and the letter of branching among a formula the flameproofing agent of the electrolytic solution for lithium cells which is shown by) and which is trialkyl phosphate — being related —; — it is related with the method of carrying out flameproofing of the electrolytic solution for lithium cells of making this flameproofing agent containing 15% of the weight or more in the solvent of the electrolytic solution again

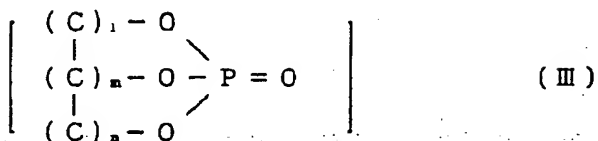
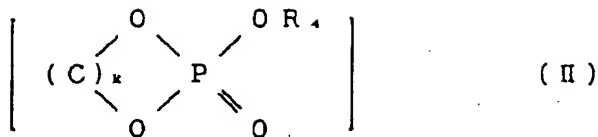
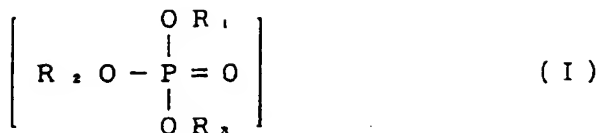
[0009] In the electrolytic solution for lithium cells which dissolved lithium salt in the organic solvent, the fire-resistant electrolytic solution is obtained by using the solvent containing phosphoric ester. That is, this invention offers the flameproofing agent and the flameproofing method of making the electrolytic solution for lithium cells fire retardancy.

[0010]

[Embodiments of the Invention] The phosphoric ester to be used is the trialkyl phosphate (I) expressed with the following general formula, the monocycle formula phosphate (II) which alkyl groups combined mutually, and 2 ring type phosphate (III).

[0011]

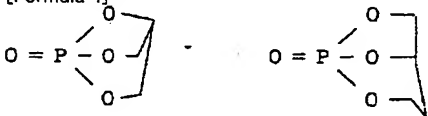
[Formula 3]



[0012] (R1-R4 are the alkyl groups of the shape of a straight chain of carbon numbers 1-4, and the letter of branching among a formula, and R1 may differ from R3 mutually.) - (C)- is a unit in the hydrocarbon group of the shape of a straight chain, and the letter of branching which has one carbon atom, and k, l, m, and n show the carbon number of this hydrocarbon group, and are k=2-8, l and m, and the integer of n=0-12.

[0013] As what is expressed with a general formula (III) to methyl-ethylene phosphate and a methyl trimethylene phosphate; row as phosphoric ester expressed with a general formula (I) as an example as trimethyl phosphate, dimethyl ethyl phosphate, methylethyl propyl phosphate, methyl diethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, and a thing expressed with tributyl phosphate; general formula (II) [0014]

[Formula 4]



[0015] And trimethylolethane phosphate etc. can be illustrated. Also in these, the direction of phosphoric ester with small molecular weight melts a solute well, and since electrical conductivity is high, it is desirable. Since the Lynn content in the molecular structure is the highest, and fire retardancy is large and does not ignite most highly electrical conductivity], especially trimethyl phosphate is the most desirable.

[0016] The phosphoric ester used by this invention is trialkyl phosphate shown by the general formula (I).

[0017] Although the rate for which it accounts to the electrolytic solution of the above-mentioned phosphoric ester changes with military requirements of a lithium cell, when a solvent is made into the whole quantity and phosphoric ester, a fire-resistant high lithium cell is obtained most. In order to add as an assistant solvent to the conventional electrolytic solution and to raise fire retardancy, if it is used 30% of the weight or more preferably, good fire retardancy will be acquired 15% of the weight or more.

[0018] As a solvent which mixes the above-mentioned phosphoric ester, ether solvents, such as lactone solvent; 1, such as carbonate solvent; gamma-butyrolactone,], such as ethylene carbonate, propylene carbonate, and butylene carbonate, 2-dimethoxyethane, 1, 3-dioxolane, and a tetrahydrofuran, can be illustrated.

[0019] Moreover, as a solute, LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiCF₃SO₃, and LiAlCl₄ grade can be illustrated.

[0020]

[Example] The example of reference and the example of comparison are given to below, and this invention is explained still more concretely.

[0021] As a fire-resistant appraisal method of the electrolytic solution, the rate of combustion of the paper which sank in the electrolytic solution was adopted. The flash point was measured by the Pensky Martens closed tester.

[0022] The Manila paper of 40 micrometers in width of face of 15mm, a length of 320mm, and thickness and density 0.6 g/cm³ was dipped in the electrolytic solution (electrical conductivity 5.6 mS/cm in 25 degrees C) which dissolved LiBF₄ [with a mol concentration of 1] in example 1 trimethyl phosphate for 1 minute, for 3 minutes, it hung perpendicularly and the excessive electrolytic solution was removed. Thus, the Manila paper into which the electrolytic solution was infiltrated was immediately extinguished in less than 10mm of combustion distance, when it fixed at a level with the sample maintenance base which has a support needle at intervals of 25mm and the end was lit in a match.

[0023] When asked for the rate of combustion from time to dip Manila paper in the electrolytic solution (electrical conductivity 7.8 mS/cm in 25 degrees C) which dissolved LiBF₄ [with a mol concentration of 1] in example of comparison 1 gamma-butyrolactone on the same conditions as an example 1, and burn 300mm by the same ignition examination, the rate of combustion was 10 mm/s.

[0024] In an example 2 and three examples 1, the solvent was changed into the mixed solvent (example 3) of the weight ratio 1:1 of triethyl phosphate (example 2), and gamma-butyrolactone and trimethyl phosphate, and the same ignition examination was performed. All showed high fire retardancy.

[0025] In the example 1 of example of comparison 2 comparison, when the solvent was changed into propylene

carbonate and the same examination was performed, it was a flammability.

[0026] The same ignition examination was performed about the Manila paper which does not sink in at all as the example 1 of reference - an example 1 of 7 reference, and the Manila paper which sank in only the solvent as examples 2-7 of reference.

[0027] The result of these ignition examinations; the electrical conductivity of flash point [of each example, the example of comparison, and the example (except for example 1 of reference) sample of reference]; and each example, and the example sample of comparison is summarized in a row, and it is shown in Table 1.

[0028] In addition, the following cable address was used in Table 1.

GBL: Gamma-butyrolactone PC: Propylene-carbonate TMP:trimethyl-phosphate TEP:triethyl phosphate TBP: Tributyl phosphate. [0029]

[Table 1]

表 1

No.	電解液又は溶媒	燃焼速度 V(mm/s)	引火点 fp(°C)	電気伝導度(25°C) σ (mS/cm)
実施例 1	LiBF ₄ /TMP	0*	>150	5.6
" 2	LiBF ₄ /TEP	0*	113	5.8
" 3	LiBF ₄ /GBL+TMP(1:1)	0*	103	8.0
比較例 1	LiBF ₄ /GBL	10	100	7.8
" 2	LiBF ₄ /PC	7	135	4.0
参考例 1	なし	11	—	—
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" 3	TEP	0*	113	—
" 4	TPP	0*	138	—
" 5	TBP	0*	132	—
" 6	GBL	20	96	—
" 7	PC	19	131	—

(注) * : 燃焼 10 mm 以内で消火

[0030]

[Effect of the Invention] It became possible to obtain the electrolytic solution which shows the fire retardancy which was excellent in the solubility of a lithium salt solute, and was suitable and excellent in the electrolytic solution of a lithium cell with this invention.

[0031] The electrolytic solution for lithium cells of this invention is used as the electrolytic solution of the high lithium cell of safety, especially a portable lithium cell.

[Translation done.]

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TECHNICAL FIELD

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PRIOR ART

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[0003] On the other hand, the organic compound which contains lithium or a halogen in a molecule as an inorganic compound, such as an antimony oxide and boric-acid zinc, is known as a flameproofing agent. However, in case fire retardancy is given to the electrolytic solution, it is necessary not to bar the fundamental performance as the electrolytic solutions, such as conformity between conductivity, the operating potential range, operating temperature limits, and an electrode material. For example, in almost all cases, an above-mentioned inorganic compound and an above-mentioned halogenide are a solid matter, are insoluble in an organic solvent, and reduce conductivity. Moreover, halogenated hydrocarbons, such as a methylene chloride currently generally used as an organic solvent, have a low dielectric constant, and since conductivity is reduced, they cannot be used as a solvent used for the electrolytic solution.

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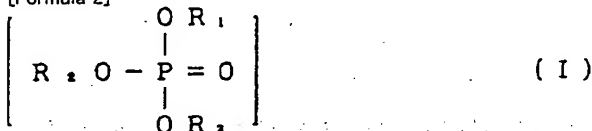
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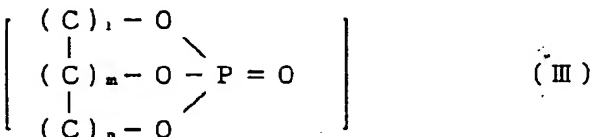
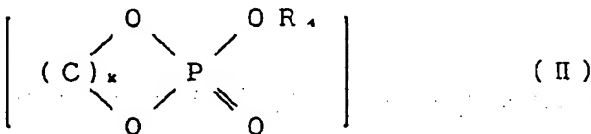
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[0019] Moreover, as a solute, LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiCF_3SO_3 , and LiAlCl_4 grade can be illustrated.

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(注) * : 燃焼 10 mm 以内で消火

[Translation done.]

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(12) 公開特許公報 (A)

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(74) 代理人 弁理士 津国 肇

(54) 【発明の名称】 リチウム電池用電解液の難燃化剤

(57) 【要約】

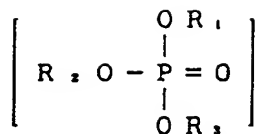
【課題】 リチウム電池の電解液を難燃化する難燃化剤及び難燃化方法を提供する。

【解決手段】 アルキル基が炭素数1～4の直鎖状又は分枝状であるトリアルキルホスフェートを含有する、リチウム電池用電解液の難燃化剤；ならびにそのトリアルキルホスフェートを電解液の溶媒中に50重量%以上含有させ、又は溶媒の全量として含有させる、リチウム電池用電解液を難燃化する方法。

(2)

【特許請求の範囲】

【請求項1】 一般式 (I) :



* 【化1】

*

(式中、R₁~R₃は、互いに同一でも異なってもよい、炭素数1~4の直鎖状又は分枝状のアルキル基である。)で示されるトリアルキルホスフェートである、リチウム電池用電解液の難燃化剤。

【請求項2】 R₁~R₃がメチル基である、請求項1記載の難燃化剤。

【請求項3】 電解液の溶媒中に、請求項1又は2記載の難燃化剤を15重量%以上含有させる、リチウム電池用電解液を難燃化する方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リチウム電池に用いる電解液に関する。本発明によれば、安全性の高いリチウム電池を得ることができる。

【0002】

【従来の技術】従来、リチウム電池には、電解液として、プロピレンカーボネート、γ-ブチロラクトン、1,2-ジメトキシエタンなどの単独又はこれらの混合溶媒に、過塩素酸リチウム、ホウフッ化リチウム、リンフッ化リチウム、トリフルオロメタンスルホン酸リチウムなどの溶質を溶解したものが使用されている。

【0003】一方、難燃化剤として、酸化アンチモンやホウ酸亜鉛などの無機化合物ならびに分子中にリン又はハロゲンを含む有機化合物などが知られている。しかし、電解液に難燃性を付与する際には、電気伝導率、※

※使用電位範囲、使用温度範囲、電極材料との間の適合性など、電解液としての基本的性能を妨げないことが必要となる。たとえば、上述の無機化合物やハロゲン化合物は、ほとんどの場合固体物質であり、有機溶媒に不溶で、電気伝導率を低下させる。また一般に有機溶媒として使用されている塩化メチレンなどのハロゲン化炭化水素は、誘電率が低く、電気伝導率を低下させるので、電解液に使用する溶媒としては使用できない。

【0004】

【発明が解決しようとする課題】上記のリチウム電池は、非常に燃え易い溶媒を使用しているため、内部短絡等によって電池が破壊した際に、火花が電解液に引火して、機器を損傷したり、火災に至ることがあり得る。特に、近年、携帯用機器にリチウム電池が搭載されるようになり、リチウム電池の安全性はますます重要性を増し、社会問題と成りつつある。

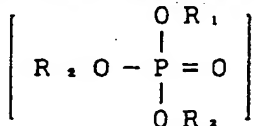
【0005】

【課題を解決するための手段】本発明者は、低級リン酸エステルを電解液の溶媒あるいは助溶媒として利用することにより、電池としての特性を維持しつつ、難燃性を示す電解液を得ることに成功し、本発明を完成した。

【0006】すなわち、本発明は、一般式 (I) :

【0007】

【化2】



(I)

【0008】(式中、R₁~R₃は、互いに同一でも異なってもよい、炭素数1~4の直鎖状又は分枝状のアルキル基である。)で示されるトリアルキルホスフェートである、リチウム電池用電解液の難燃化剤に関し;また電解液の溶媒中に、該難燃化剤を15重量%以上含有させる、リチウム電池用電解液を難燃化する方法に関する。

【0009】リチウム塩を有機溶媒に溶解したリチウム電池用電解液において、リン酸エステルを含んだ溶媒を使用することにより、難燃性電解液が得られる。すなわ

ち本発明は、リチウム電池用の電解液を難燃性にする難燃化剤及び難燃化方法を提供するものである。

【0010】

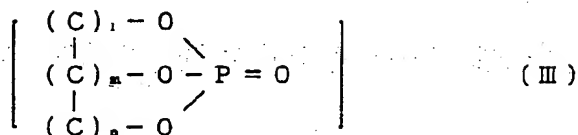
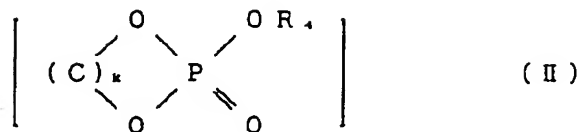
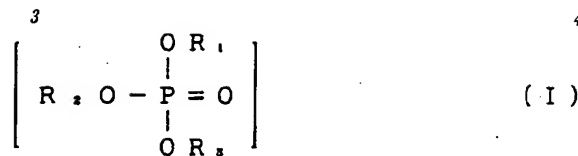
【発明の実施の形態】使用するリン酸エステルは、下記の一般式で表わされるトリアルキルホスフェート

(I)、アルキル基どうしが互いに結合した単環式ホスフェート(II)及び二環式ホスフェート(III)である。

【0011】

【化3】

(3)



【0012】(式中、 $\text{R}_1 \sim \text{R}_4$ は炭素数1~4の直鎖状又は分枝状のアルキル基で、 $\text{R}_1 \sim \text{R}_3$ は互いに異なってもよい。—(C)—は、直鎖状又は分枝状の炭化水素基における、1個の炭素原子を有する単位であり、 k, l, m, n は、該炭化水素基の炭素数を示し、 $k = 2 \sim 8, l, m, n = 0 \sim 12$ の整数である。)

【0013】具体例としては、一般式(I)で表わされるリン酸エステルとしてトリメチルホスフェート、ジメチルエチルホスフェート、メチルエチルプロピルホスフェート、メチルジエチルホスフェート、トリエチルホスフェート、トリプロピルホスフェート、トリブチルホスフェート；一般式(II)で表わされるものとして、メチルエチルホスフェート、メチルトリメチルホスフェート；ならびに一般式(III)で表わされるものとし

て、

【0014】

【化4】



【0015】及びトリメチロールエタンホスフェート等を例示することができる。これらの中でも、分子量の小さいリン酸エステルの方が、溶質を良く溶かし、電気伝導度が高いので好ましい。特にトリメチルホスフェートは、電気伝導度が最も高く、また、分子構造中のリン含有量が最も高いために、難燃性が大きくて引火しないので、最も好ましい。

【0016】本発明で用いるリン酸エステルは、一般式(I)で示されるトリアルキルホスフェートである。

【0017】上記のリン酸エステルの電解液に占める割合は、リチウム電池の要求性能によって異なるが、溶媒

を全量、リン酸エステルにした場合に最も難燃性の高いリチウム電池が得られる。従来の電解液に助溶媒として添加して難燃性を向上させるためには、15重量%以上、好ましくは30重量%以上使用すると、良好な難燃性が得られる。

【0018】上記のリン酸エステルを混合する溶媒としては、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート等のカーボネート溶媒； γ -ブチロラクトン等のラクトン溶媒；1,2-ジメトキシエタン、1,3-ジオキソラン、テトラヒドロフラン等のエーテル溶媒を例示することができる。

【0019】また、溶質としては、 LiClO_4 、 LiBF_4 、 LiPF_6 、 LiAsF_6 、 LiCF_3SO_3 、 LiAlCl_4 等を例示することができる。

【0020】

【実施例】以下に参考例及び比較例を挙げて、本発明をさらに具体的に説明する。

【0021】電解液の難燃性の評価法として、電解液を含浸した紙の燃焼速度を採用した。引火点は、ペンスキー・マルテンス密閉式試験器によって測定した。

【0022】実施例1

トリメチルホスフェートに LiBF_4 を1モル濃度溶解した電解液(25℃における電気伝導度5.6mS/cm)に、幅15mm、長さ320mm、厚さ40 μm 、密度0.6g/cm³のマニラ紙を1分間浸し、3分間、垂直に吊上げて余分な電解液を除いた。このようにして電解液を含浸させたマニラ紙を、25mm間隔で支持針を有するサンプル保持台に水平に固定して、その一端にマッチで着火したところ、燃焼距離10mm以内でただちに消火した。

【0023】比較例1

γ -ブチロラクトンに LiBF_4 を1モル濃度溶解した電解液(25℃における電気伝導度7.8mS/cm)に、実施例1と同じ条件でマニラ紙を浸し、同様の着火試験

(4)

5

6

によって、300mm燃焼する時間より燃焼速度を求めたところ、燃焼速度は10mm/sであった。

【0024】実施例2、3

実施例1において、溶媒をトリエチルホスフェート（実施例2）、 γ -ブチロラクトンとトリメチルホスフェートとの重量比1：1の混合溶媒（実施例3）に変えて、同様の着火試験を行った。いずれも高い難燃性を示した。

【0025】比較例2

比較例1において、溶媒をプロピレンカーボネートに変えて、同様の試験を行ったところ、易燃性であった。

【0026】参考例1～7

参考例1として何も含浸しないマニラ紙、参考例2～7として溶媒のみを含浸したマニラ紙について、同様の着*

* 火試験を行った。

【0027】これらの着火試験の結果；ならびに各実施例、比較例、参考例（参考例1を除く）試料の引火点；及び各実施例、比較例試料の電気伝導度をまとめて表1に示す。

【0028】なお、表1では次の略号を使用した。

GBL： γ -ブチロラクトン

PC：プロピレンカーボネート

TMP：トリメチルホスフェート

TEP：トリエチルホスフェート

TBP：トリブチルホスフェート

【0029】

【表1】

表1

No.	電解液又は溶媒	燃焼速度 V(mm/s)	引火点 fp(°C)	電気伝導度(25°C) σ (mS/cm)
実施例1	LiBF ₄ /TMP	0*	>150	5.6
" 2	LiBF ₄ /TEP	0*	113	5.8
" 3	LiBF ₄ /GBL+TMP(1:1)	0*	103	8.0
比較例1	LiBF ₄ /GBL	10	100	7.8
" 2	LiBF ₄ /PC	7	135	4.0
参考例1	なし	11	—	—
" 2	TMP	0*	なし	—
" 3	TEP	0*	113	—
" 4	TPP	0*	138	—
" 5	TBP	0*	132	—
" 6	GBL	20	96	—
" 7	PC	19	131	—

(注) *：燃焼10mm以内で消火

【0030】

【発明の効果】本発明により、リチウム塩溶質の溶解性に優れてリチウム電池の電解液に適し、かつ優れた難燃性を示す電解液を得ることが可能になった。

【0031】本発明のリチウム電池用電解液は、安全性の高いリチウム電池、とくに携帯用のリチウム電池の電解液として用いられる。